2009 Abstract of Master Thesis

Energies and excited-state dynamics of the $1B_u^+$, $1B_u^-$ and $3A_g^-$ states of carotenoids bound to LH2 antenna complexes from purple photosynthetic bacteria

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[Introduction] Light-harvesting systems of purple bacteria contain bacteriochlorophylls (BChls) and carotenoids (Cars). BChls play a key role in efficient absorption of light and transfer of excitation energy to the reaction centers [1]. Cars serve as *accessory* light-harvesting pigments and, on the other hand, as triplet quenchers to provide protection against photooxidative damage [2]. Recently, pump-probe spectroscopy of Cars (n = 9–13) in solution using ~30 fs pulses (temporally short but spectrally broad) was shown to excite simultaneously and coherently closely located pairs of diabatic levels [3]. The current investigation was done with the purpose to examine if the same type of phenomena can be observed with Cars (n = 9–11) that are bound to light-harvesting complexes from purple photosynthetic bacteria, i.e., if similar coherent excitation of the diabatic vibronic levels and similar excited-state dynamics occur in the set of Cars bound to the light-harvesting complexes.

[Experimental] Peripheral light harvesting complexes 2 (LH2) from *Rhodobacter (Rba.) sphaeroides* G1C, *Rba. sphaeroides* 2.4.1 and *Rhodospirillum (Rsp.) molischianum* have been prepared as described previously [4] with some modifications. The set-up and the method for femtosecond time-resolved absorption spectroscopy were as described previously (Supporting Information of Ref. [5]) except for some modifications for white-light continuum generation: The strongest 550-nm laser pulses from a TOPAS-White (Quantronix) of low energy was focused onto a 1-mm glass plate to generate a white-light continuum probe pulse by the use of a pair of concave reflection mirrors with a focal length of ~5 cm. As a result, the full width at half-maximum (FWHM) of the cross-correlation traces between the pump and probe pulses (~30 fs) was determined to be ~60 fs using the optical Kerr-effect signal.

[Results and Discussion]

Compared to Cars in solution, Cars bound to antenna complexes exhibit stronger stimulated emission from the optically-forbidden $1B_u^-(0)$ and $3A_g^-(0)$ levels, as well as spectrally broader stimulated emission from the $1B_u^+(0) + X^-(\upsilon)$ diabatic pair. It was also found, that the low-energy shift of stimulated emission signals from the covalent $1B_u^-(0)$ and $3A_g^-(0)$ levels was larger than that from the ionic $1B_u^+(0)$ state. The results suggest that the polarization of the Cars' conjugated chain is increased in LH2. More efficient triplet generation in Cars bound to LH2 additionally suggests a twisting of the conjugated chain.

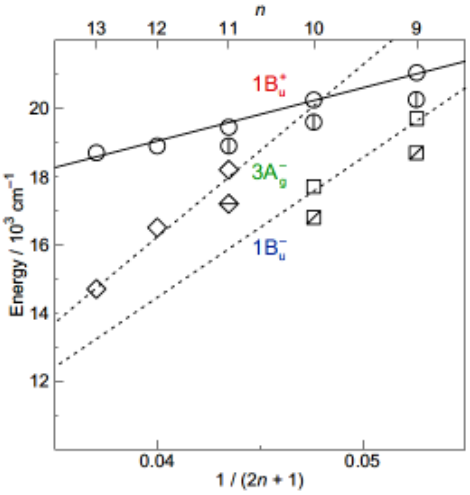

Fig. 1. Comparison of the 1Bu+(0), 1Bu–(0) and 3Ag–(0) energies determined for Cars bound to LH2 from *Rba. sphaeroides* G1C, 2.4.1 and *Rsp. molischianum* (crossed symbols) and those determined for Cars in THF solution (open symbols).

[References]

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[3] Miki, T.; Kakitani, Y.; Koyama, Y.; Nagae, H. Stimulated emission from the $1B_u^-(0)$ level and the $1B_u^+(0) + 1B_u^-$ (1 and 2) diabatic levels upon excitation to the $1B_u^+(0)$ level in neurosporene and spheroidene. *Chem. Phys. Lett.* **2008**, *457*, 222–226.

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